

The theoretical fuel consumption of an ideal apparatus is 405,000 B. t. u. per barrel. The writer believes that an efficiency of 50 to 60 per cent should be attainable in practice by use of special rotary kilns, and this would correspond to a fuel consumption of 674,000 to 810,000 B. t. u. per barrel.

In Figure 9 are assembled three curves showing the output or fuel economy characteristics of three types of rotary kilns which are furnished with regenerative coolers that utilize the secondary air to abstract 100,000 B. t. u. per barrel from the hot clinker. A comparison of curves 2 and 1 shows the advantage of increasing the length of the kiln while keeping the diameter inside the brickwork constant. The longer kiln shows a better fuel economy at all outputs and the fuel economy is less affected by output than is the case with the shorter kiln. Curve 3 shows the curve for a special type of rotary kiln, proposed by the writer, in which devices are installed for improving heat transfer between the incoming raw mix and the outgoing gases in the upper 40 feet of the kiln. It is not the purpose at this time to describe the mechanical features of this improved type of kiln, but merely to call attention to the possibilities for greater fuel economy which result from effi-

cient countercurrent heat transfer between gas and raw mix in the upper end of the kiln.

Figure 10 shows curves for a kiln of 8.5 feet inside diameter in its principal length by 240 feet long, and for the same kiln equipped with the special devices for improving countercurrent heat transfer in the upper end of the kiln proposed by the writer. These curves again bring out the fact that in the usual types of kilns of given length the 6-foot kiln has a better fuel economy than the 8.5-foot kiln; but the latter has a much greater output. The final fact which interests the engineer is actual commercial economy, and it is quite possible that under usual conditions the 8.5 by 240 foot kiln will be more economical in a commercial sense than a 6 by 240 foot kiln. This is a problem involving all commercial factors, including cost of fuel, labor, power, money, and the respective investments per barrel per day of output. Such a study must pertain only to each special case, and is out of place here. The special device will give substantially the same fuel economy to the 8.5 by 240 foot kiln as to the 6 by 240 foot kiln, but the relative burden put upon these devices is greater in the former than the latter.

Methanol from Hydrogen and Carbon Monoxide II—Dimethyl Ether¹

Ralph L. Brown and A. E. Galloway

PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, PITTSBURGH, PA.

A RECENT report² presented a general comparison of the conversion into methanol of carbon monoxide and hydrogen under pressure by zinc oxide and the basic and normal zinc chromates. At 400° C. and under the conditions of the experiments the normal zinc chromate was found to be the most active. Work on this catalyst has been extended to other temperatures, and a closer inquiry has been made into the liquid products obtained. The results constitute the material of this paper.

Production of Methanol and Methyl Ether

Employing the apparatus and procedure previously described,² the hourly production of methanol at temperatures between 300° and 400° C. and at 180 atmospheres average reactant pressure was determined for space velocities of 3000 and 7500. The initial gas contained on an average of 32+ per cent carbon monoxide and about twice that amount of hydrogen. The catalyst was prepared as previously described,² and the amount used was 250 cc. (248 grams). The results are given in Table I.

In Figure 1 the data from columns 2 and 5 of Table I have been plotted on the figure (No. 10) employed in the earlier paper² to show the three values at 400° C. and a curve of estimated yields obtained by the Nernst approximation formula used empirically. The new data give experimental conversion curves for space velocities of 3000 and 7500. It is evident from these curves that the conversions, at low space

The production of methanol from a 2:1 hydrogen-carbon monoxide mixture at 180 atmospheres pressure has been studied between 300° and 400° C. with normal zinc chromate as the catalyst. At a space velocity of 3000 the conversion of the carbon monoxide to methanol was found to increase from about 7 per cent to a maximum of about 30 per cent at 375° C. and then to decline to 20 per cent at 400° C. Dimethyl ether has been shown to be a by-product of the reaction, being formed from the methanol in amounts which increase with temperature between 300° and 400° C.

velocities and with side reactions excluded, would be greater than the "estimated" curve indicates. During this work close attention has been paid to the character of the side reactions. An important one is the formation of dimethyl ether.

Evidences of Formation of Dimethyl Ether

In seeking, during the early stages of the work on methanol, a possible reason for some of the divergence between the conversions demanded by the calculated equilibrium constants of Kelley³ and those obtained experimentally by the writers at 400° C., the possibility of side reactions and their by-products was considered.

The tendency to dehydrate as well as to dehydrogenate alcohols is shown by many metallic oxides, and the fact that these properties overlap (coexist) is well known. Many of the oxides have been classified by Sabatier⁴ according to these two tendencies into a dehydrating, dehydrogenating, and a mixed group, which is by far the largest of the three; at the dehydrating end of the mixed group is placed chromic oxide, and the last member of the group of mixed behavior next to the dehydrogenating group is zinc oxide. The question might be raised as to whether under certain conditions there is really more than the one group—the mixed group. Although rigid application of decomposition data to synthetic prediction is to be avoided, the reverse of the dehydrogenating influence is utilized in the synthesis of methanol with the aid of pressure, and it is evident that the dehydration of the methanol formed

¹ Received September 21, 1928. Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

² Brown and Galloway, *IND. ENG. CHEM.*, **20**, 960 (1928).

³ Kelley, *IND. ENG. CHEM.*, **18**, 78 (1926).

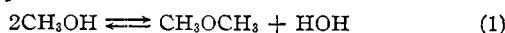
⁴ Sabatier-Reid, "Catalysis in Organic Chemistry," 1st ed., D. Van Nostrand Co., p. 696.

might well occur at the same time. This dehydration involves no change in the number of molecules and therefore is little affected directly by pressure. In this dehydration, both chromic and zinc oxides might be expected to function to some degree; whereas aluminum oxide, if present, should be fairly active in the conversion of methanol to methyl ether.

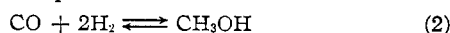
Table I—Methanol and Ether Production with Normal Zinc Chromate

RUN	AV. TEMP.	SPACE VELOCITY	PURE CH ₃ OH	CONVERSION CO TO CH ₃ OH PER PASS	DIMETHYL ETHER			
					Total for run	Liquid products	Equivalent methanol	Conversion CO to ether per pass
	° C.		G./hr.	%	Grams	%	G./hr.	%
A	300	3000	27.6	7.0	1.0	1.65	0.7	1.0
B	307	3000	29.7	9.1	1.9	1.95	1.1	1.2
C	311	3000	38.1	10.9	4.8	2.95	3.34	1.7
D	350	3000	83.3	22.5	4.2+	2.75	3.8	0.7
E	350	7500	100.2	13.2	8.0	5.45	7.4	3.3
F	375	3000	95.6	28.94	5.6	4.45	7.8	1.2
G	375	7500	123.5	16.4	7.5	8.6	8.4	5.2+
H	397	3000	68.0	21.4	...	...	...	...
I	398	3000	72.4	20.5	...	...	...	...

While this study was in progress, Adkins and Perkins⁵ published the results of their study of the behavior (at 1 atmosphere) of methanol over aluminum and zinc oxides. They reported the formation by zinc oxide of small but definite amounts of dimethyl ether from methanol⁶ between 325° and 400° C.; in other words, the experimental evidence of the catalytic activity of zinc oxide in the alcohol to ether dehydration was presented. If this fact is accepted, the extent to which it may occur during the pressure synthesis of methanol depends upon the equilibrium



However, the concentration of the methanol is also primarily conditioned by the equilibrium constants in the reaction



In the case of reaction 1 McKee and Burke⁷ have determined $K_p = \frac{(\text{CH}_3\text{OH})^2}{\text{CH}_3\text{OCH}_3 \times \text{H}_2\text{O}} = 0.32$ (about) at 350° C. This means that at 350° C. equilibrium would exist when 78 per cent of the original methanol had been converted into methyl ether and at 300° C. it would be about 80 per cent. This represents the limit, and the actual conversion depends on the activity of the methanol catalyst employed and the time of contact. These considerations apply equally well to attempts to determine equilibrium constants for the methanol reaction at 1 atmosphere and to similar experiments at high pressures. For example, in reaction 2, at 180 atmospheres reactant pressure and 350° C., and at equilibrium, the ratio of CO to CH₃OH (calculated to CO) is about 1:1, whereas in reaction 1, occurring at the same time and assuming equilibrium according to McKee and Burke, the ratio of CH₃OH to CH₃OCH₃ (calculated to CH₃OH equivalents) is 22:78. Similarly at 300° C. the two ratios would be, respectively, about 20:80 and 20:80 (equivalent to a molecular ratio CH₃OH:CH₃OCH₃ of 1:2). In both cases the methanol catalysts (oxides) are highly active in the methanol reaction, which is rapid and much less active under the same conditions (as the writers' experimental data on zinc chromate indicate) with respect to ether formation (reaction 1). As stated above and evidenced by the writers' experimental data, the latter reaction in the case of zinc chro-

mate is greatly affected by the time of contact. In the pressure synthesis of methanol the space velocities are relatively high and the time of contact short, thus favoring the methanol reaction and limiting the formation of ether.

However, with a mixed or a double catalyst to furnish high activity with respect to both reactions 1 and 2, the results should offer broad and interesting possibilities. It would mean that water gas under pressure passed over such a catalyst or catalysts would issue—reduced in volume, to be sure—but with a materially enhanced heating value due to the ether present in it and containing a recoverable quantity of methanol. There is a present-day interest in the distribution of a dry domestic gas, and in the event of its realization increasing the heating value of water gas by the catalytic formation of dimethyl ether (which gasifies at -23.65° C.) seems to be a technical possibility.

The possibilities of ether formation at atmospheric pressure and very slow space velocities, and its influence in the determination of the methanol-water gas equilibrium are interesting to consider. If, in the absence of established equilibrium values, we assume for the sake of discussion that

$K_p = \frac{\text{CH}_3\text{OH}}{\text{CO} \times \text{H}_2^2}$ at 300° C. = 60.6×10^{-8} , then the ratio of CO to CH₃OH (as CO) at 300° C. is 99.973 to 0.027; and as before the ratio of CH₃OH, as such, to the methanol that has been converted to ether is, at equilibrium, 20:80 or 1:4. The amount of ether that could be formed, although large with respect to the methanol, is yet so small that its influence on the ratio of carbon monoxide to methanol which measures the equilibrium is unimportant.

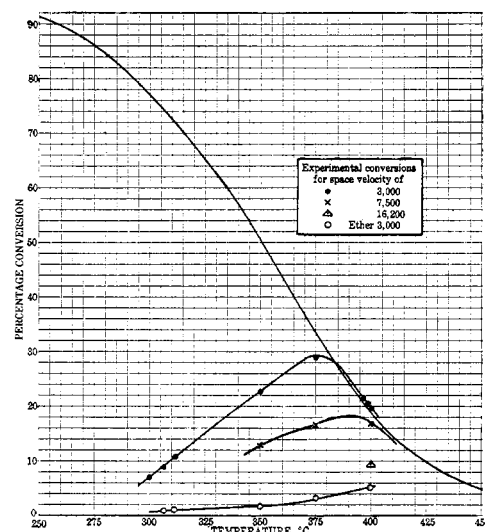


Figure 1—Percentage of Carbon Monoxide Converted to Methanol and Methyl Ether at 180 Atmospheres

In addition to these theoretical considerations, there were several indirect evidences of ether formation. One was the apparently large amount of gas set free by the methanol when it was drawn from the receiver under pressure into a receiver at room temperature and 1 atmosphere. Another was the character of the distillation curves showing the purity of the synthetic methanol, as given in the earlier paper.² In those samples produced at 400° C. there was, in addition to a higher percentage of water, a corresponding increase in the amount of the crude methanol, which distilled slightly under the true boiling point of methanol. In the same samples the loss in volume due to distillation was likewise indicative of a volatile constituent. A further indication was the fact that in the carbon monoxide balances there was an apparent

⁵ Adkins and Perkins, *J. Phys. Chem.*, **32**, 221 (1928).

⁶ The presence of ethylene among their gaseous products from methanol when the reaction was carried out at higher temperatures over alumina is extremely interesting, both in connection with Nef's "methylene" theories and also in view of the production of higher alcohols from carbon monoxide and hydrogen by catalysts containing aluminum oxide, as by Lewis and Frolich, *IND. ENG. CHEM.*, **20**, 354 (1928).

⁷ McKee and Burke, *IND. ENG. CHEM.*, **15**, 682, 788 (1923).

loss on the effluent side of the catalyst or among the products plus the residual carbon monoxide.

Examination of Methyl Ether

In addition to the foregoing evidences experimental data were sought. The first test showed that the amounts of methanol vapors and methyl ether being lost in the residual

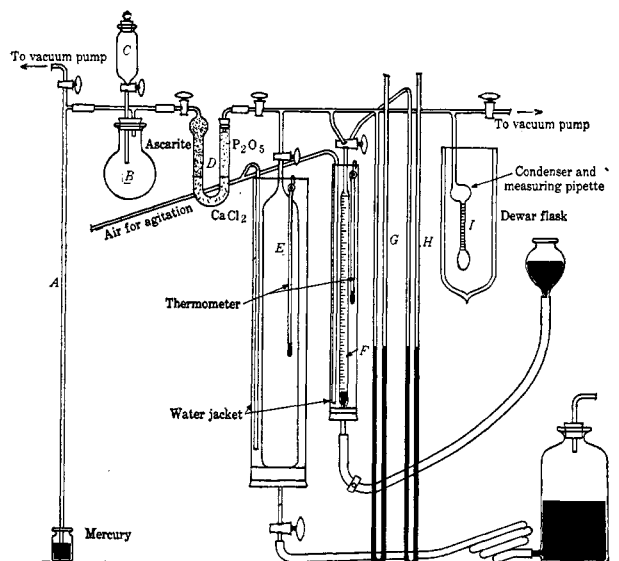


Figure 2—Apparatus Used in Examination of Methyl Ether

gas under the usual procedure were negligible. Provision was then made to examine more closely the gases released when the methanol at 0° C. or below was delivered from the pressure receiver to a flask for weighing. These gases were sampled after being passed through a collecting tube cooled to -80° C., and then through concentrated sulfuric acid.

In the tube a liquid was condensed, which proved to be largely dimethyl ether. This liquid on fractionation gave a small amount of residue, methanol, and a relatively large portion of a liquid which was condensed in a tube containing metallic sodium to remove any methanol or water that still might remain in it. It was then distilled and passed into sulfuric acid at 0° C., in which it was very largely absorbed. The unabsorbed gas would neither burn nor support combustion. It was principally carbon dioxide and contained a little air from the system of glass.

The ether that was collected in sulfuric acid had the characteristic odor and the proper boiling point of dimethyl ether. It was a gas at room temperatures, was free from unsaturated hydrocarbons (before the sulfuric acid absorption), and boiled at -23.5° C., which excluded the presence of any appreciable amount of saturated hydrocarbons. Its solubility in cold sulfuric acid⁶ (over 400 per cent by liquid volume at 0° C.) and almost complete release on addition of water is characteristic.⁸ The identification was concluded by determining the relation of the volume of the gas under standard conditions to its liquid volume, and from that result calculating its molecular weight, density, and other properties. The perfect conformance of these characteristics with those of dimethyl ether fixed its identity fully.

⁶ Erdmeyer and Kruchbaumer, *Ber.*, **7**, 699 (1874).

The gas thought to be dimethyl ether was liberated from the sulfuric acid (B, Figure 2), thoroughly dried over phosphorus pentoxide in D, and then passed into a system which had been well evacuated. The gas was confined over clean mercury in water-jacketed burets—one, E, of exactly 1090 cc. capacity, and the second, F, of 50 cc. capacity and graduated in a standard manner. An exact volume of the gas confined in the system was condensed in a small bulb, T, of known volume with a calibrated capillary stem connecting it to the burets. The volume of this condensed liquid could be read accurately to within ± 0.001 cc. when it was between 2.5 and 3.0 cc., and it was so arranged. As given in Table II, the volume of the condensed liquid was read at various temperatures between about -80° C. and its boiling point, which was noted in each of two chargings of gas to be about -23.5° C. The liquid in the bulb was allowed to evaporate back into the burets and the gas volume again read.

Table II—Experimental Data on Identification of Methyl Ether

TEMPERATURE (COR.)		VOLUME		BAROMETRIC PRESSURE
Gas	Liquid	Gas	Liquid	
° C.	° C.	Cc.	Cc.	Mm.
Initial:				
25.3	...	1104.6	...	740
25.2	...	1103.4	...	740
...	-79.0	...	2.530	...
...	-79.0	...	2.533	...
...	-55.0	...	2.644	...
...	-53.8	...	2.654	...
...	-53.0	...	2.659	...
...	-52.0	...	2.664	...
...	-39.0	...	2.730	...
...	-38.0	...	2.734	...
...	-34.0	...	2.759	...
...	-32.0	...	2.768	...
...	-30.0	...	2.780	...
...	-28.0	...	2.790	...
...	-26.0	...	2.801	...
...	-25.0	...	2.805	...
...	-24.0	...	2.810	...
...	-23.0	...	2.814	...
Final:				Boiling
25.18	...	1104.7	...	739.2+
25.20	...	1105.1	...	739.2+

CALCULATIONS—The data of columns 2 and 4 of Table II give us the graph in Figure 3, from which we read the volume of liquid at -23.65° C. to be 2.812 cc. The data of Cardoso and Coppola⁹ were plotted and extrapolated below 0° C.,

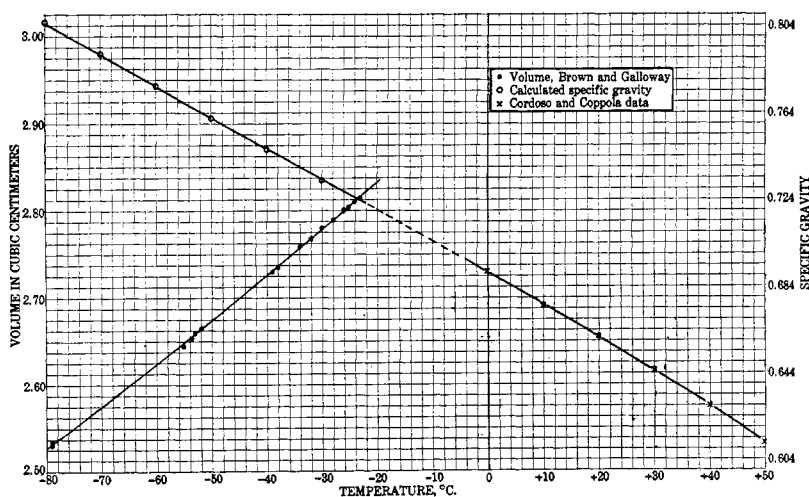


Figure 3—Approximate Volume-Temperature Relationship and Specific Gravity of Methyl Ether, -20° to -80° C.

from which the specific gravity of dimethyl ether is found to be 0.7240 at -23.65° C. Hence, if pure ether, the 2.812 cc. of liquid would weigh 2.036—grams.

The total volume of gas obtained from this amount of liquid was 986.8 cc. at 0° C. and 760 mm., which multiplied by

⁹ Cardoso and Coppola, *J. chim. phys.*, **20**, 337 (1923).

46.046/23,379¹⁰ = 2.0304 grams (or 2.805— cc. at $-23.67^{\circ}\text{C}.$). The 2.036— grams is equivalent to 2.063 grams per liter at $0^{\circ}\text{C}.$ and 760 mm., to 2.1155 for L_0 (when $1 + \lambda = 1.0254$) and a mol weight of 46.17, compared, respectively, to 2.0576, 2.1098, and 46.046 as given in the International Critical Tables. The agreement is better than 3 parts in 1000, which represents approximately the accuracy of the apparatus and procedure, and it completes the identification of the material as dimethyl ether.

Notwithstanding the fact that the data of Table II, which are intended for identification purpose only, have not the accuracy of precision measurements, the writers have employed them to give the approximate specific gravities of dimethyl ether between -80° and $-20^{\circ}\text{C}.$ These have been found useful in converting directly the volumes of liquid ether collected into grams. They were calculated from the extrapolated gravity of 0.7240 at $-23.65^{\circ}\text{C}.$ and the temperature-volume relationship represented in Figure 3 in which these approximate specific gravities are likewise graphed.

¹⁰ Values from International Critical Tables, Vol. III, p. 4, and represent weight of 1 cc. or the molecular weight divided by true gram-molecular volume of methyl ether.

Extent of Ether Production in Methanol Synthesis

The data on the dimethyl ether produced between 300° and $400^{\circ}\text{C}.$ as a by-product of the methanol synthesis (with normal zinc chromate as the catalyst) are given in Table I. This production of ether calculated as carbon monoxide converted to ether is shown graphically by the lower curve in Figure 1.

The extent to which this ether formation affects the values for percentage conversions of carbon monoxide to methanol in Table I is not very great. Under the experimental conditions employed, the formation of ether is slow compared with the methanol reaction, and if the carbon monoxide converted ultimately to ether is subtracted from the carbon monoxide which enters the catalyst chamber, the correction is about $+0.6$ per cent for the conversions in runs F and H and negligible in the others.

The influence of time of contact is evident from the data of Table I for $350^{\circ}\text{C}.$ At space velocities of 3000 and 7500 the ether found was, respectively, 1.42 and 0.71 grams per pass. Similarly, at $375^{\circ}\text{C}.$ the production was 3.16 and 1.47 grams for the same respective space velocities.

Petroleum Wash-Oil Thickening in the Scrubbing of Coke-Oven Gas¹

H. M. Ullmann, D. S. Chamberlin, C. W. Simmons, and M. A. Thorpe

LEHIGH UNIVERSITY, BETHLEHEM, PA.

A HIGH-BOILING petroleum oil is used in the counter-current absorption of light oils from coke-oven gas in scrubbing towers. With continued use the wash oil increases in gravity from 0.834 to 0.90 and contains a suspension which, when settled out, does not materially affect the gravity of the oil. This process is called thickening. With thickening, a wash oil reduces in absorption capacity and the accumulation of the suspended material presents mechanical difficulties throughout the entire system. It is the object of this investigation to determine the primary cause of such thickening.

Cause of Thickening

Kiemstedt² in 1925 summarized the suggested causes of thickening as follows:

- (1) The oxygen content of the gases and its influence on the wash oil, especially on the phenols of the wash oils.
- (2) The oxidation of hydrogen sulfide to sulfur and its asphalt-forming property.
- (3) The capacity of oils for inorganic materials, especially compounds of iron and their catalytic influence on the process.
- (4) The moisture content of the oils.
- (5) Cracking.
- (6) The prevailing pressure on the system.

In 1926 Hilgenstock³ pointed out that "even at this late date no satisfactory explanation has been given for thickening."

Offe,⁴ and Kattwinkel,⁵ although disagreeing as to the mechanism of thickening, point to hydrogen sulfide as the primary cause. Offe states that the thickening is caused by

the reaction of hydrogen sulfide with the unsaturated compounds present in the wash oil and their subsequent polymerization by heat with the regeneration of hydrogen sulfide. Kattwinkel, however, views the thickening as due to polymerization of the wash oil by sulfuric and sulfo acids formed from the oxidation of the hydrogen sulfide present. Since hydrogen sulfide is present in the coke-oven gas to the extent of 500 grains per 100 cubic feet, such reasons seem quite logical. In addition, the wash oil on thickening increases in sulfur content from 0.182 to 0.967 per cent.

All attempts to thicken a new wash oil with hydrogen sulfide were unsuccessful. No thickening resulted when hydrogen sulfide was bubbled through cold or hot oil for 3 weeks, or when a saturated solution of the gas in the oil was subjected to a treatment similar to that given in the stripping stills and heat exchangers. Even when steel wool was used as a catalyst and the above processes duplicated, there was no thickening. In some cases, however, there was a slight and insignificant increase in the sulfur content of the wash oil after treatment.

Another suggested mechanism is that thickening may be the result of sulfur as such, being produced in the system by the reduction of hydrogen sulfide. If was found, however, that flowers of sulfur, although dissolving in hot oil, would precipitate on cooling and produce no thickening.

It has been suggested that thickening may be produced by cracking of the wash oil in the stripping process. Experiments with new wash oil, benzolized wash oil, and wash oil saturated with hydrogen sulfide and flowers of sulfur, all produce no thickening when heated to a cracking temperature. In every case a black, carbonaceous residue is precipitated and the light fractions formed volatilize, but the residual oil does not increase in gravity.

According to Bergbau and Lothringen⁶ the thickening may be due to oxygen or carbon dioxide, or both, since their method

¹ Received May 28, 1928. Revised manuscript received November 7, 1928.

² Kiemstedt, *Brennstoff-Chem.*, **6**, 185, 201 (1925).

³ Hilgenstock, *Ibid.*, **7**, 123 (1926).

⁴ Offe, *Gas Wasserfach*, **66**, 67 (1923); **68**, 136 (1925).

⁵ Kattwinkel, *Ibid.*, **67**, 406, 474 (1924); **68**, 323 (1925); *Brennstoff-Chem.*, **7**, 123 (1926).

⁶ Bergbau and Lothringen, German Patent 432,378 (January 3, 1924).